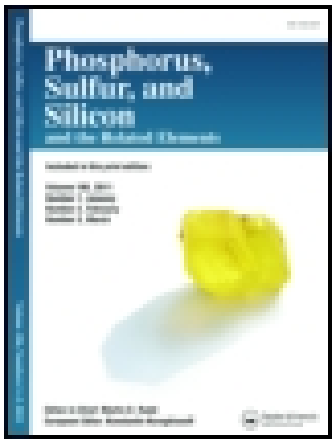


Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gpss20

CARBAMOYL AND THIOCARBAMOYL DERIVATIVES OF N-BENZYL-AMINOMETHYL-DIMETHYL-PHOSPHINE OXIDE

Emil Tashev [a], Viktoria Lachkova [b], Helmut Keck [c], Stoycho Shenkov [a], Wolfgang Kläui [c] & Sabi Varbanov [a]

[a] Institute of Polymers, Bulgarian Academy of Sciences, Sofia, Bulgaria

[b] Department of Ecology, Sofia, Bulgaria

[c] Department of Inorganic Chemistry and Structural Chemistry, Düsseldorf, Germany

Published online: 16 Aug 2010.

To cite this article: Emil Tashev, Viktoria Lachkova, Helmut Keck, Stoycho Shenkov, Wolfgang Kläui & Sabi Varbanov (2004) CARBAMOYL AND THIOCARBAMOYL DERIVATIVES OF N-BENZYL-AMINOMETHYL-DIMETHYL-PHOSPHINE OXIDE, Phosphorus, Sulfur, and Silicon and the Related Elements, 179:9, 1757-1767, DOI: 10.1080/10426500490466364

To link to this article: http://dx.doi.org/10.1080/10426500490466364

Phosphorus, Sulfur, and Silicon, 179:1757–1767, 2004

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500490466364

CARBAMOYL AND THIOCARBAMOYL DERIVATIVES OF N-BENZYL-AMINOMETHYL-DIMETHYL-PHOSPHINE OXIDE

Emil Tashev,[a] *Viktoria Lachkova,*[b] *Helmut Keck,*[c] *Stoycho Shenkov,*[a] *Wolfgang Kläui,*[c] *and Sabi Varbanov*[a]
Institute of Polymers, Bulgarian Academy of Sciences, Sofia, Bulgaria;[a] *Department of Ecology, Forestry University, Sofia, Bulgaria;*[b] *and Department of Inorganic Chemistry and Structural Chemistry, Heinrich-Heine University—Düsseldorf, Düsseldorf, Germany*[c]

(Received December 30, 2003; accepted January 8, 2004)

A series of thirteen new carbamoyl and thiocarbamoyl derivatives of N-benzyl-aminomethyl-dimethyl-phosphine oxide have been synthesized and characterized. The compounds were prepared via interaction of N-benzyl-aminomethyl-dimethyl-phosphine oxide with the corresponding isocyanates or isothiocyanates. The composition of the synthesized novel compounds was proved by elemental analysis for nitrogen and the structures were confirmed by IR, ^{1}H*-,* ^{31}P*-* $^{31}P\{^{1}H\}$ *NMR spectroscopy and by mass spectrometry.*

Keywords: N-Benzyl-aminomethyl-dimethyl-phosphine oxide; N-substituted-carbamoyl-(or thiocarbamoyl-)-N-benzyl-aminomethyl-dimethyl-phosphine oxides; phosphorus-containing ureas and thioureas; tertiary phosphine oxides

INTRODUCTION

Tertiary phosphine oxides functionalized with primary or secondary amino groups and diesters of aminophosphonic acids are very interesting as starting reagents for preparation of new organophosphorus compounds.[1–4] The highly reactive amino groups included in such compounds allow the preparation of a great number of derivatives, such as ureas, nitrosoureas, thioureas, Shiff bases, adducts with oxyranes and bisoxyranes, and coordination compounds with metal ions.[4–10] Some

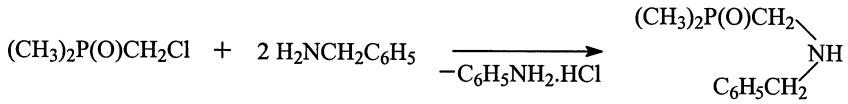
The paper is dedicated to the memory of Professor Gueorgui Borissov.

Address correspondence to S. Varbanov, Institute of Polymers, Bulgarian Academy of Sciences, BG-1113 Sofia, Bulgaria. E-mail: varbanov@polymer.bas.bg

of these derivatives have shown physiological activity, even antitumor activity.[7,11–13] This article is a continuation of our investigations on the preparation of carbamoyl and thiocarbamoyl derivatives based on tertiary phosphine oxides, functionalized with primary or secondary amino groups and diesters of aminophosphonic acids.[4–6] We report here the synthesis and characterization of N-substituted carbamoyl-(or thiocarbamoyl)-N-benzyl-aminomethyl-dimethylphosphine oxides **1–13** (Table I), which are expected to exhibit biological activity and complex formation properties with metal ions.

RESULTS AND DISCUSSIONS

The starting secondary phosphorus-containing monoamine N-benzyl-amino-methyl-dimethyl-phosphine oxide (BAPO) was prepared via substitution of the chlorine atom in dimethyl-chloromethyl-phosphine oxide according to Scheme 1.

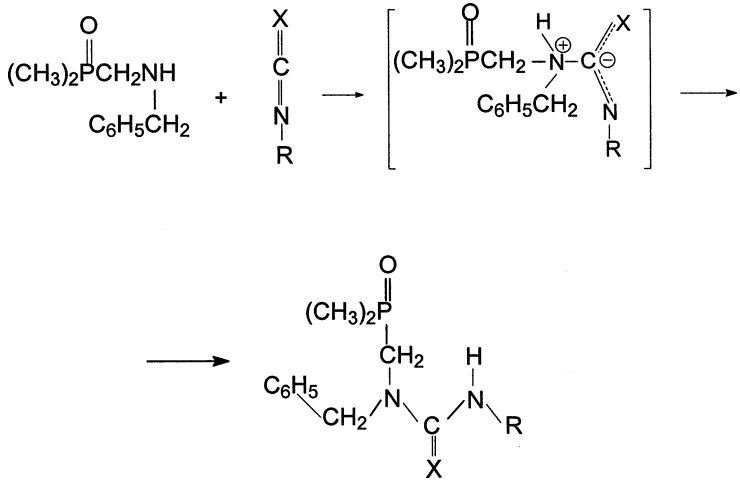


SCHEME 1

The preparation of BAPO from the same starting compounds was marked by Maier[2] and Schmutzler and coworkers,[14,15] and was used for synthetic purposes, but the synthesis, identification, and characterization of the compound was not described. The BAPO is a solid, white crystal and a hygroscopic substance soluble in alcohols, diethyl ether, tetrahydrofurane, ethylacetate, DMFA, DMSO, toluene, dichloromethane, and chloroform, and insoluble in aliphatic hydrocarbons (hexane, heptane) and water. The nuclear magnetic resonance (NMR) data in $CDCl_3$ (presented in the experimental part) confirm the structure of the compound.

The carbamoyl- and thiocarbamoyl derivatives **1–13** (Table I) were synthesized by nucleophilic addition of BAPO to the corresponding isocyanates and isothiocyanates according to Scheme 2.

The interaction between the reagents was realized as described previously by us[5,6] in dichloromethane solution at room temperature with molar ratio of the reagents of 1:1. The products were isolated by filtration after crystallization from the reaction mixture and washing with dry diethyl ether, and recrystallized from ethanol or ethanol-ethylacetate mixture. All reported new carbamoyl and thiocarbamoyl derivatives have been prepared with almost quantitative



SCHEME 2

yields (Table II). The interaction between the reagents proceeds with an exothermal effect. These two facts indicate that N-benzyl-aminomethyl-dimethyl-phosphine oxide is a strong nucleophilic agent, similar to the primary phosphorus-containing monoamine, aminomethyl-dimethyl-phosphine oxide,[1] and the secondary phosphorus-containing monoamine with two phosphine oxide groups in the molecule, bis(dimethyl-phosphinyl-methyl)amine.[3]

Some preparative and analytical data for the compounds **1–13** are shown in Table II. All compounds are white crystalline substances that melt at high temperatures. They are soluble in DMSO and DMFA, less soluble in dichloromethane, chloroform, acetone, and methanol, sparingly soluble in diethyl ether, tetrahydrofuran, and dioxane, and insoluble in aliphatic and aromatic hydrocarbons. The composition of **1–13** was established by elemental analysis for nitrogen (Table II). Their structures were confirmed by IR-, ^{1}H-, ^{31}P-, and ^{31}P{^{1}H}-NMR spectroscopy and mass spectrometry.

The infrared spectra of **1–13** (Table III) showed characteristic bands assigned to the phosphoryl group (P=O) at 1141–1178 cm^{-1}, methyl groups bonded to a phosphorus atom (CH_3-P) at 1294–1331 cm^{-1}, bands of the carbonyl groups (C=O) involved in hydrogen bonds at 1634–1657 cm^{-1} (Amide I), and intensive bands of the thiocarbonyl group (C=S) at 933–939 cm^{-1} and at 1246–1295 cm^{-1} (corresponding to Amide I). Bands for amide (NH—C=O) and thioamide (NH—C=S) groups at 1528–1547 cm^{-1} (Amide II) and several bands for N—H at 3025–3386 cm^{-1} are present as well. Characteristic bands for aromatic

TABLE I Molecular Structure of Carbamoyl and Thiocarbamoyl Derivatives **1–13** of N-benzyl-aminomethyl-dimethyl-phosphine Oxide

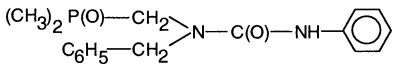
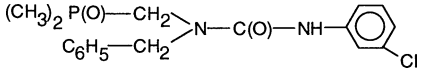
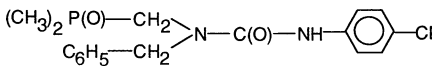
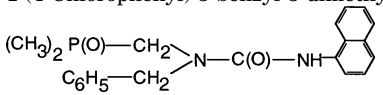
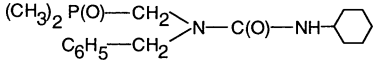
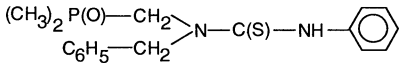
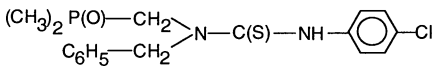
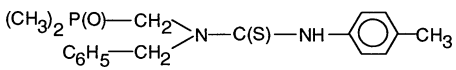
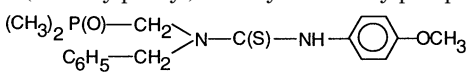
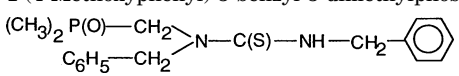
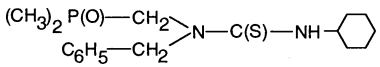
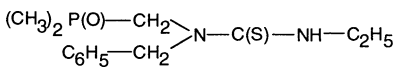
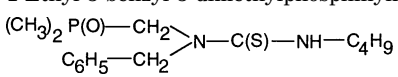
No.	Compounds
1	
	1-Phenyl-3-benzyl-3-dimethylphosphinylmethyl-urea
2	
	1-(3-Chlorophenyl)-3-benzyl-3-dimethylphosphinylmethyl-urea
3	
	1-(4-Chlorophenyl)-3-benzyl-3-dimethylphosphinylmethyl-urea
4	
	1-(1-Naphthyl)-3-benzyl-3-dimethylphosphinylmethyl-urea
5	
	1-Cyclohexyl-3-benzyl-3-dimethylphosphinylmethyl-urea
6	
	1-Phenyl-3-benzyl-3-dimethylphosphinylmethyl-thiourea
7	
	1-(4-Chlorophenyl)-3-benzyl-3-dimethylphosphinylmethyl-thiourea
8	
	1-(4-Methylphenyl)-3-benzyl-3-dimethylphosphinylmethyl-thiourea
9	
	1-(4-Methoxyphenyl)-3-benzyl-3-dimethylphosphinylmethyl-thiourea
10	
	1,3-Dibenzyl-3-dimethylphosphinylmethyl-thiourea
11	
	1-Cyclohexyl-3-benzyl-3-dimethylphosphinylmethyl-thiourea
12	
	1-Ethyl-3-benzyl-3-dimethylphosphinylmethyl-thiourea
13	
	1-n-Butyl-3-benzyl-3-dimethylphosphinylmethyl-thiourea

TABLE II Preparative and Analytical Data of Carbamoyl and Thiocarbamoyl Derivatives **1–13** of N-benzyl-aminomethyl-dimethyl-phosphine Oxide

No	Yield, %	Melting point,°C	General formula, mol. mass	Nitrogen, %	
				Found	Calcd.
1	96	176–177	$C_{17}H_{21}N_2O_2P$, 316,34	8.95	8.86
2	98	148–149.5	$C_{17}H_{20}ClN_2O_2P$, 350,78	7.82	7.99
3	99	188–189	$C_{17}H_{20}ClN_2O_2P$, 350,78	7.81	7.99
4	92	222–224	$C_{21}H_{23}N_2O_2P$, 366,40	7.52	7.65
5	97.7	163–165	$C_{17}H_{27}N_2O_2P$, 322,39	8.54	8.69
6	96	169–170	$C_{17}H_{21}N_2OPS$, 332,40	8.58	8.43
7	98	167–168	$C_{17}H_{20}ClN_2OPS$, 367,85	7.79	7.64
8	97	159–161	$C_{18}H_{23}N_2OPS$, 346,43	7.95	8.09
9	99	164–165	$C_{18}H_{23}N_2O_2PS$, 362,43	7.64	7.73
10	96	144–145	$C_{18}H_{23}N_2OPS$, 346,43	7.96	8.09
11	94	173–174	$C_{17}H_{27}N_2OPS$, 338,45	7.15	7.21
12	99	173.5–174.5	$C_{13}H_{21}N_2OPS$, 284,36	9.76	9.85
13	98	124–124.5	$C_{15}H_{25}N_2OPS$, 312,41	8.85	8.97

rings were at 1490–1503 cm^{-1} and 1588–1602 cm^{-1}. The bands of the phosphoryl groups (P═O) of **1–13** are shifted with 30–50 cm^{-1} to the lower frequencies when compared to nonsubstituted tertiary phosphine oxides, which is due to their association with N─H amide and thioamide protons via hydrogen bonds.[16] Some of the compounds **1–13** show two bands for the phosphoryl group. This phenomenon could be ascribed to different spatial isomers or two kinds of phosphoryl groups: the first one bonded with hydrogen bond, while the second one did not bond.[16]

The bands of CH_2 groups in the cyclohexane ring are at 883, 2850, and 2933 cm^{-1} for the compound **5** and at 877, 2859, and 2924 cm^{-1} for the compound **12**. The bands for monosubstituted Ar-rings in **8** and **9** are at 742 cm^{-1} and 735 cm^{-1}, respectively.

The NMR data correspond to the structure of the prepared compounds (Table IV). The ^{1}H-NMR study of **1–13** showed resonance signals as doublets for CH_3─P═O at 1.30–1.51 ppm and $^2J_{HP}$ = 12.6–13.2 Hz. The resonance signals of the methylene protons CH_2-P═O were registered as broad singlets for thiocarbamoyl compounds **6–13** at 4.00–4.24 ppm and as doublets for **1–5** carbamoyl compounds at 3.58–3.82 ppm with $^2J_{HP} = 3.1–5.4$ Hz. The resonance signals for Ar─CH_2─N protons were singlets at 4.58–5.24 ppm. The resonances for NH─C(X) amide or thioamide protons were broad singlets at a wide region from 5.37 ppm for **5** to 9.91 ppm for **7**. These signals disappear or their integral intensity is significantly reduced after deuterium exchange with CD_3OD, which is a relatively slow process at room temperature even

TABLE III Characteristic IR Data (ν, δ, cm^{-1}) for Carbamoyl and Thiocarbamoyl Derivatives **1–13** of N-benzyl-aminomethyl-dimethyl-phosphine Oxide

No	ν(P═O)	$\nu(CH_3P)$	$\nu(CH_2)$	ν(C═O)	ν(C═S)	δ(HN—C═O)	δ(HN—C═S)	ν(N—H)	ν (Ar)
1	1149 (m)	1304 (m)	1445 (s)	1657 (vs)	—	1543 (s)	—	3241 (m)	1500 (s)
	1166 (s)	1312 (m)							1597 (s)
2	1171 (vs)	1310 (m)	1432 (s)	1649 (vs)	—	1541 (s)	—	3273 (m)	1490 (s)
									1594 (s)
3	1157 (s)	1302 (s)	1415 (s)	1651 (vs)	—	1538 (vs)	—	3228 (s)	1491 (s)
	1178 (vs)		1472 (m)						1593 (s)
4	1151 (vs)	1295 (m)	1452 (m)	1634 (s)	—	1528 (vs)	—	3386 (s)	1503 (vs)
		1307 (m)		1650 (s)				3512 (m)	1600 (s)
5[a]	1160 (vs)	1304 (m)	1454 (m)	1639 (vs)	—	1542 (vs)	—	3299 (s)	—
	1170 (vs)		1474 (s)						
6	1141 (s)	1303 (m)	1449 (m)	—	937 (s)	—	1531 (vs)	3027 (m)	1496 (s)
	1154 (vs)		1477 (m)		1267 (m)			3186 (s)	1600 (m)
7	1157 (vs)	1331 (m)	1418 (m)	—	935 (m)	—	1537 (s)	3198 (m)	1492 (vs)
					1295 (m)				1588 (m)
8[b]	1153 (vs)	1295 (m)	1476 (s)	—	939 (vs)	—	1530 (vs)	3025 (w)	1495 (m)
		1311 (m)			1266 (m)			3182 (s)	1590 (w)
9[b]	1151(vs)	1295 (m)	1408 (m)	—	935 (s)	—	1530 (vs)	3186 (s)	1495 (s)
			1480 (m)		1246 (vs)				1602 (w)
10	1150 (vs)	1304 (m)	1408 (m)	—	934 (s)	—	1543 (vs)	3263 (s)	1495 (m)
			1452 (m)		1274 (m)				1600 (w)
11[a]	1133 (vs)	1301 (s)	1410 (s)	—	934 (s)	—	1546 (vs)	3266 (s)	—
	1163 (vs)		1455 (m)		1254 (m)				
12	1169 (vs)	1331 (m)	1397 (s)	—	935 (s)	—	1547 (vs)	3265 (s)	—
			1455 (m)		1290 (m)				
13	1124 (m)	1294 (m)	1397 (s)	—	933 (s)	—	1539 (vs)	3272 (s)	—
	1163 (vs)	1304 (m)	1456 (m)		1269 (m)				

[a)]The bands of CH_2 groups in the cyclohexane ring: comp. No **5** at 883 (m), 2850 (m), 2933 (s); No **12** at 877 (s), 2859 (m), 2924 (s) cm^{-1}.

[b)]Bands for monosubstituted Ar-ring: comp. No **8** at 742 (s) cm^{-1} and No **9** at 735 (s) cm^{-1}.

TABLE IV ^{1}H and $^{31}P\{^{1}H\}$ NMR Data of Carbamoyl and Thiocarbamoyl Derivatives **1–13**[a] of N-benzyl-aminomethyl-dimethyl-phosphine Oxide (δ in ppm, J in Hz)

	^{1}H NMR, Protons							
Comp. no.	$(CH_3)_2P(O)$		$CH_2P(O)$		$Ar—CH_2N$	R—NH—C(X)	Ar—H	$^{31}P\{^{1}H\}$
	δ	$^{2}J_{HP}$	δ	$^{2}J_{HP}$	δ	δ	δ	δ
1	1.41 (d)	12.6	3.62 (d)	3.7	4.64 (s)	8.74 (s)	7.17–7.33 (m)	+45.73
2	1.40 (d)	12.6	3.58 (d)	4.4	4.61 (s)	9.23 (s)	6.90–7.48 (m)	+46.18
3	1.39 (d)	12.6	3.58 (d)	3.7	4.61 (s)	9.17 (s)	7.14–7.33 (m)	+46.14
4	1.51 (d)	13.2	3.82 (d)	5.4	4.80 (s)	8.24 (s)	7.19–7.74 (m)	+45.29
5[b]	1.41 (d)	12.6	3.61 (d)	3.1	4.58 (s)	5.37 (s)	7.16–7.30 (m)	+44.96
6	1.49 (d)	12.6	4.08 (bs)	—	5.21 (s)	9.51 (s)	7.07–7.35 (m)	+46.29
7	1.48 (d)	12.6	4.00 (bs)	—	5.24 (s)	9.91 (s)	7.19–7.30 (m)	+46.68
8[c]	1.49 (d)	12.6	4.12 (bs)	—	5.23 (s)	9.25 (s)	7.05–7.35 (m)	+46.18
9[d]	1.49 (d)	12.6	4.14 (bs)	—	5.23 (s)	9.15 (s)	6.78–7.35 (m)	+46.14
10[e]	1.48 (d)	12.6	4.24 (bs)	—	5.08 (s)	7.02 (s)	7.09–7.30 (m)	+45.30
11[f]	1.47 (d)	12.6	4.17 (bs)	—	5.06 (s)	6.76 (s)	7.17–7.31 (m)	+45.44
12[g]	1.46 (d)	12.6	4.08 (bs)	—	5.09 (s)	7.05 (s)	7.18–7.30 (m)	+45.60
13[h]	1.46 (d)	12.6	4.13 (bs)	—	5.08 (s)	7.00 (s)	7.18–7.31 (m)	+45.54

[a]Abrevations: bs, broad singlet; d, doublet; m, multiplet; s, singlet; t, triplet.

[b]The signal for cyclohexane CH_2 protons of the compound were as five multiplets at 0.94–1.85 ppm. The signal for cyclohexane CH proton was a multiplet at 3.45–3.57 ppm.

[c]The signal for CH_3—Ar protons was at 2.25 (s) ppm.

[d]The signal for CH_3O—Ar protons was at 3.72 (s) ppm.

[e]The signal for methylene Ar—CH_2—N—C(S) was at 4.75 (d) and $^{3}J_{HH} = 5.06$ Hz, because of the coupling with NH—C(S) thioamide proton. After deuterium exchange with CD_3OD it changes to a singlet.

[f]The signals for cyclohexane CH_2 protons were as five multiplets at 0.99–1.99 ppm. The signal for cyclohexane CH proton was a multiplet at 4.13–4.20 ppm and overlapped with the resonance signal for $CH_2P(O)$ protons.

[g]The resonace signal for ethyl CH_3 protons was at 1.08 (t) ppm with $^{3}J_{HH} = 7.25$ Hz. The resonance signal for ethyl CH_2 protons was a multiplet at 3.53–3.58 ppm.

[h]The resonance signals for butyl protons were respectively at: CH_3-C—C—C—NH—C(S) at 0,80 (t) ppm with $^{3}J_{HH} = 7.55$ Hz, C—CH_2—C—C—N—C(S) at 1.19 (m) ppm, C—C—CH_2C—N—C(S) at 1.43–1.47 (m) ppm and the signal overlapped with the resonance signal for $(CH_3)_3P(O)$ protons and for C—C—C—CH_2N—C(S) at 3.49–3.55 (m) ppm.

in homogenous solution of $CDCl_3$ and CD_3OD. The resonances of both kinds of the aryl protons were observed as multiplets at range 6.78–7.74 ppm.

The resonances of methyl (CH_3-P), methylene (CH_2-P), and (Ar—CH_2—N) protons of the carbamoyl derivatives **1–5** are in stronger field than the resonances of the same proton of thiocarbamoyl derivatives **6–13**.

The $^{31}P\{^1H\}$-NMR and ^{31}P-NMR spectra of the carbamoyl and thiocarbamoyl derivatives **1–13** represent singlet or multiplet resonance signals in the range from +45.29 to +46.68 ppm, respectively, which is typical for tertiary phosphine oxides containing one methylene and two methyl groups at the phosphorus atom.[17]

Mass spectrometric data (EI: 70 eV) that confirm the proposed structures and elemental compositions of the compounds, are presented in Table V. In all mass spectra, signals due to molecular ions can be found. The fragmentations of $[M]^{+\cdot}$ can easily been understood. The N—C(X) bond seems to be very labile, and the main fragmentation pathway is loss of C(X)NHR under formation of $[(CH_3)_2P(O)CH_2NCH_2C_6H_5]^+$ m/z 196. Peaks due to fragmentation within the substituents R are of no importance. All spectra show abundant signals for $[CH_2NH(CH_2C_6H_5]^+$ (m/z 120) that has been formed by elimination of $CH_3(CH_2)PO$ (−76u) and $[NH(CH_2C_6H_5]^+$ (m/z 106), which is generated by elimination of $CH_3(CH_2)PO(CH_2)$ (−90u) from the ion m/z 196 and H-migration to the nitrogen atom.The base peak in all spectra is m/z 91. It belongs to $[C_7H_7]^+$—a typical fragment in mass spectra of compounds containing a C_6H_5—CH_2 substituent.

EXPERIMENTAL

Starting Materials

The used isocyanates and isothiocyanates were commercially available products from Fluka (Switzerland) and Merck (Germany), while chloromethyl-dimethyl-phosphine oxide was purchased from Hoechst AG (Germany). The solvents were dried by standard procedures before use.

Characterization of the Prepared Compounds 1–13

The elemental analysis for nitrogen content was performed according to the method of Dumas. The melting points were measured on a Boetzius microheating plate PHMK05 (Germany) and were uncorrected.

The infrared spectra (400–4000 cm^{-1}) were recorded on a Bruker Vector-22 infrared (IR) spectrometer as KBr pellets.

TABLE V Significant Mass Spectrometric Data (EI) for the Carbamoyl and Thiocarbamoyl Derivatives of N-benzyl-aminomethyl-dimethyl-phosphine Oxide (rel. Int. % (m/z))

	Compound no.												
Fragments	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**
$[M]^{+\cdot}$	10 (360)	4 (350)	7 (350)	11 (366)	14 (322)	10 (322)	4 (366)	4 (346)	21 (362)	17 (346)	30 (338)	50 (284)	27 (312)
$[(CH_3)_2P(O)CH_2NCH_2C_6H_5]^+$	3	15	4	10	12	12	5	8	3	24	70	62	56
$[CH_2NH(CH_2C_6H_5]^+$ (m/z 120)	39	25	39	62	96	45	36	32	50	29	45	32	26
$[NH(CH_2C_6H_5]^+$ (m/z 106)	21	12	16	25	51	31	20	19	25	51	52	59	61
$[C_7H_7]^+$ (m/z 91)	100	100	100	100	100	100	100	100	100	100	100	100	100

The ^{1}H-NMR spectra were taken on a Bruker Advance DRX 500 spectrometer at 500.13 MHz in $CDCl_3$. The chemical shifts are given relative to internal TMS (tetramethylsilane). The ^{31}P and $^{31}P\{^1H\}$ NMR spectra were registered in the same solvent on the same instrument at 202.45 MHz. The chemical shifts are given relative to external 85% aqueous H_3PO_4.

EI-mass spectra [EI-MS] were measured at 70 eV, source temperature 200°C, using the direct inlet system on a Finnigan MAT 8200 mass spectrometer.

Procedure for the Preparation of N-Benzyl-aminomethyl-dimethyl-phosphine Oxide

A mixture of dimethyl-chloromethyl phosphine oxide (12.7 g, 0.10 mol) benzylamine (24.5 g, 0.23 mol), and xylene (150 ml) was refluxed for 12 h in argon atmosphere. The formed benzylamine-hydrochloride was removed by filtration, and the xylene was evaporated at reduced pressure. The crude yellowish oil was dissolved in 150 ml chloroform, and after filtration the solution was washed twice with water. After drying with Na_2SO_4, the solvent was evaporated and the product distilled at 152–154°C/0.3 Torr. Yield 86% (17.1 g). The product melts at 30–35°C. ^{1}H-NMR: $\delta = 7.24$–7.33 (m, 5H, Ar—H), $\delta = 3.86$ (s, 2H, CH_2-N, $\delta = 2.86$ (d, 2H, CH_2-P, $^2J_{HP} = 7{,}3$ Hz), $\delta = 2.21$ (s, 1H, NH), $\delta = 1.49$ (d, 6H, $(CH_3)_2$-P, $^2J_{HP} = 12.6$ Hz). $^{31}P\{^1H\}$-NMR: $\delta = +43.53$ (s).

General Procedure for the Preparation of Carbamoyl and Thiocarbamoyl Derivatives 1–13

A solution of isocyanate or isothiocyanate (4.0 mmol) in dichloromethane (1.0 ml) was added dropwise to a stirred solution of N-benzyl-aminomethyl-dimethyl-phosphine oxide (4.0 mmol) in dry dichloromethane (3.0 ml) at room temperature. An exothermal reaction was observed, and the reaction mixture was stirred at room temperature until a solid product was obtained, which was then allowed to stay for 2 h. In some cases the reaction mixture was stirred at 30–40°C for 15 min and approximately 1 ml of hexane or diethylether added and cooled. The crude products were separated by filtration, washed with diethyl ether, and recrystallized from ethanol or ethanol-ethylacetate mixture to a constant melting point. The preparative and analytical data of **1–13** are presented in Table II.

REFERENCES

[1] S. Varbanov, G. Agopian, and G. Borisov, *Eur. Polym. J.*, **23,** 639 (1987).

[2] L. Maier, *Phosphorus, Sulfur, and Silicon*, **53,** 43 (1990).
[3] S. Varbanov, T. Tosheva, and E. Russeva, *Phosphorus, Sulfur, and Silicon*, **127,** 27 (1997).
[4] V. Lachkova, G. Petrov, and A. H. Hussein, *Phosphorus, Sulfur, and Silicon*, **85,** 161 (1993).
[5] V. Lachkova, S. Varbanov, H. Keck, and T. Tosheva, *Phosphorus, Sulfur, and Silicon*, **152,** 53 (1999).
[6] V. Lachkova, S. Varbanov, G. Hägele, H. Keck, and T. Tosheva, *Phosphorus, Sulfur, and Silicon*, **177,** 1303 (2002).
[7] R. Gugova, S. Varbanov, Z. Raikov, G. Demirov, D. Todorov, and M. Ilarionova, *Pharmazie*, **46,** 603 (1991).
[8] S. Varbanov, A. Georgieva, G. Hägele, H. Keck, and V. Lachkova, *Phosphorus, Sulfur, and Silicon*, **159,** 109 (2000).
[9] J. Klee, H. H. Hörhold, H. Schütz, S. Varbanov, and G. Borisov, *Angew. Makromol. Chem.*, **170,** 145 (1989).
[10] G. Borisov, S. Varbanov, L. M. Venanzi, A. Albinati, and F. Demartin, *Inorg. Chem.*, **33,** 5430 (1994).
[11] E. Stanoeva, S. Varbanov, V. Alexieva, I. Sergiev, V. Vasileva, M. Rashkova, and A. Georgieva, *Phosphorus, Sulfur, and Silicon*, **165,** 117 (2000).
[12] L. Maier, *Phosphorus, Sulfur, and Silicon*, **56,** 5 (1991).
[13] N. Dodoff, S. Varbanov, G. Borisov, and N. Spassovska, *J. Inorg. Biochem.*, **39,** 201 (1990).
[14] T. Kaukorat, I. Neda, R. G. Jones, and R. Schmutzler, *Phosphorus, Sulfur, and Silicon*, **122,** 33 (1997).
[15] T. Kaukorat, I. Neda, and R. Schmutzler, *Z. Naturforsch.*, **50b,** 1818 (1995).
[16] D. E. C. Corbridge, In *Topics in Phosphorus Chemistry*, edited by M. Grayson and E. J. Griffith (John Wiley & Sons, New York, 1969), Vol. 6, pp. 235–265.
[17] E. N. Tzvetkov, T. E. Kron, and M. I. Kabachnik, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1980,** 669 (1980).